

Single Molecule Photon Statistics from a Sequence of Laser Pulses

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There are many ways of calculating photon statistics in quantum optics in general and single molecule spectroscopy in particular such as the generating function method, the quantum jump approach or time ordering methods. In this paper starting with the optical Bloch equation, within the paths interpretation of Zoller, Marte and Walls we obtain the photon statistics from a sequence of laser pulses expressed by means of quantum trajectories. We find general expressions for $P_n(t)$ - the probability of emitting n photons up to time t , discuss several consequences and show that the interpretation of the quantum trajectories (i) emphasizes contribution to the photon statistics of the coherence paths accumulated in the delay interval between the pulses and (ii) allows simple classification of the terms negligible under certain physical constraints. Applying this method to the concrete example of two square laser pulses we find the probabilities of emitting 0,1 and 2 photons, examine several limiting cases and investigate the upper and lower bounds of $P_0(t)$, $P_1(t)$ and $P_2(t)$ for a sequence of two strong pulses in the limit of long measurement times. Implication to single molecule non-linear spectroscopy and theory of pairs of photons on demand are discussed briefly.

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INTRODUCTION

The interaction of matter with a sequence of laser pulses is a powerful tool frequently used for the investigation of a wide variety of chemical, physical and biological systems [1]. This field of research called non-linear spectroscopy uses clever design of laser pulses for the investigation of fast dynamics (e.g. pico - seconds) of ensembles of molecules in the condensed phase. Recently van Dijk et al [2] reported the first experimental study of an ultra-fast pump-probe single molecule system. Unlike the previous approaches to such non-linear spectroscopy where only the ensemble average response to the external fields is resolved, the new approach yields direct information on single molecule dynamics, gained through the analysis of photon counting statistics [3]. In [3] we considered the non-linear spectroscopy for a single molecule undergoing stochastic spectral diffusion process. Here we neglect all dephasing and spectral diffusion effects, and concentrate on the effect of the laser field parameters on the photon statistics.

Another related application is the generation of two indistinguishable photons using two short laser pulses interacting with a single molecule or atom [4]. Numerous applications for such photon sources have been proposed [5, 6, 7, 8, 9] for the investigation of entangled states between identical photons and quantum properties of light, in the field of quantum information and quantum computation requiring consecutive photons to have identical wave packets. Usually in the mentioned experiments the single emitter is requested to supply one or two photons within as short as possible time interval. Although it is well established how to generate two photons from two ideal π -pulses if the delay

interval between the pulses is very long, we can never produce two photons with probability equal 1, when the interaction time is finite. Thus, the information on the upper and lower bounds of the probabilities of emitting 0, 1 and 2 photons as a function of the laser field parameters, obtained in the manuscript, can be very useful.

Although the theory of single particle photon statistics is well established [10, 11], it remained unapplied due to the absence of experimental ability to check the results. Recent experimental achievements [2, 4, 8, 12] allowed the investigation of the interaction of a single quantum system with an external laser field inspiring further development of theoretical methods [3, 13, 14, 15, 16, 17, 18]. Today there are several approaches to photon counting statistics such as generating function method [19] or quantum jump approach [20] suitable for analytical predictions and numerical calculations. In this paper we follow the path interpretation approach of Mollow and Zoller, Marte and Walls [10, 11] of the optical Bloch equations [21], and show that this method is very useful for the analysis of single molecule non-linear spectroscopy.

In what follows we consider a two level molecule interacting with two laser pulses and obtain general expressions for $P_n(t)$ - the probability of emitting n photons in interval $(0, t)$ by means of quantum trajectories. We discuss the influence of the coherence on the photon statistics. Also the explicit calculation of P_0 , P_1 and P_2 - the probabilities of emitting 0,1 and 2 photons in the limit of long measurement times ($t \rightarrow \infty$) is investigated in detail using the example of two identical square pulses. Some technical details skipped in the text are given in Appendixes A, B and C.

OPTICAL BLOCH EQUATIONS

Interaction of an atom or a molecule with a radiation field is described by the optical Bloch equations under well established conditions [21], and we remind the reader some of the basic assumptions. First (i) the laser field is intense, so that it can be modeled classically. Here the external electric field is $\mathbf{E}(t) = \mathbf{E}_0 f(t)$, where the amplitude \mathbf{E}_0 is independent of time. (ii) The electronic states of the single emitter are modeled based on the two level system approximation. This assumption is excellent when the laser is resonating with a particular absorption frequency of the molecule, the latter being well separated from other natural frequencies of the emitter. Most single molecules have a triplet state, however the life time of the triplet is much longer than the time scales under consideration in this manuscript, and it can be neglected. (iii) The spontaneous emission process is described by the Markovian approximation, where the inverse life time of the excited state is Γ . (iv) We neglect thermal dephasing, spectral diffusion and interaction of the emitter with a thermal bath, which was partially treated in [3]. (v) Finally, we will assume that the dipole moment of the excited and ground state of the single emitter is zero, so that only the transition dipole moment of the particle is important. Assumptions (i,ii,iii,iv) are physical assumptions which are justified in many single molecule experiments at least at low temperatures [12, 22], and condition (v) is not limiting since our technique could be modified in principle to the case where excited and ground states of the molecule have a dipole.

The two level system is described by a vector composed of the density matrix elements: $\sigma = (\sigma_{ee}, \sigma_{gg}, \sigma_{ge}, \sigma_{eg})^T$. Here σ_{ee} and σ_{gg} represent the populations of the excited and ground states respectively and σ_{ge}, σ_{eg} describe the coherences, namely the off diagonal matrix elements of the density matrix, and obey $\sigma_{eg}^* = \sigma_{ge}$. The optical Bloch equation is [21]

$$\dot{\sigma} = L(t) \sigma + \hat{\Gamma} \sigma, \quad (1)$$

with

$$L(t) = \begin{pmatrix} -\Gamma & 0 & -i\Omega f(t) & i\Omega f(t) \\ 0 & 0 & i\Omega f(t) & -i\Omega f(t) \\ -i\Omega f(t) & i\Omega f(t) & i\omega_0 - \Gamma/2 & 0 \\ i\Omega f(t) & -i\Omega f(t) & 0 & -i\omega_0 - \Gamma/2 \end{pmatrix} \quad (2)$$

and

$$\hat{\Gamma} = \begin{pmatrix} 0 & 0 & 0 & 0 \\ \Gamma & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}, \quad (3)$$

where the Rabi frequency is $\Omega = -\frac{1}{\hbar} \mathbf{d}_{ge} \cdot \mathbf{E}_0$ and \mathbf{d}_{ge} is the transition dipole moment of the two level system. The operator $\hat{\Gamma}$ Eq. (3) describes direct transition from the excited to the ground state, and hence is associated with the spontaneous emission of a single photon.

The optical Bloch equation Eq. (1) does not yield a direct method for calculating the probabilities of the number of emitted photons. However starting with [10, 11] an interpretation of the optical Bloch formalism yields a tool for the calculation of photon statistics, based on the n-photon-propagators (see details below). The formal solution to Eq. (1) may be given by the infinite iterative expansion in $\hat{\Gamma}$ [15, 19]:

$$\sigma(t) = \mathcal{G}(t, 0) \sigma_{(0)} + \int_0^t dt_1 \mathcal{G}(t, t_1) \hat{\Gamma} \mathcal{G}(t_1, 0) \sigma_{(0)} + \int_0^t dt_2 \int_0^{t_2} dt_1 \mathcal{G}(t, t_2) \hat{\Gamma} \mathcal{G}(t_2, t_1) \hat{\Gamma} \mathcal{G}(t_1, 0) \sigma_{(0)} + \dots, \quad (4)$$

where $\sigma_{(0)}$ is the initial condition, and the Green function describing the evolution of the system in the absence of spontaneous transitions into the ground state (i.e. without $\hat{\Gamma}$) is

$$\mathcal{G}(t, t') = \hat{T} \exp \left[\int_{t'}^t L(t_1) dt_1 \right], \quad (5)$$

where \hat{T} is the time ordering operator. The first term in the expansion Eq. (4) does not include $\hat{\Gamma}$ at all, and hence describes the process where no photons are emitted, the second term includes $\hat{\Gamma}$ just once and describes the process where one photon is emitted etc. It is therefore useful to define the conditional state $\sigma_{(t)}^{(n)}$, where n is an index for the number of photons emitted in the time interval $(0, t)$. Then by definition

$$\sigma_{(t)}^{(n)} = U_{(t,0)}^{(n)} \sigma_{(0)}, \quad (6)$$

where the n-photon-propagator [15] is

$$U_{(t,t')}^{(n)} = \int_{t'}^t dt_n \dots \int_{t'}^{t_2} dt_1 \mathcal{G}(t, t_n) \hat{\Gamma} \dots \hat{\Gamma} \mathcal{G}(t_1, t'). \quad (7)$$

The physical origin of the n-photon-propagator defined by Eq. (7) is simple and intuitive: the system evolves interacting with the laser field without photon emissions until time t_1 , it then emits a single photon and continues the evolution without emissions until time t_2 when it emits the second photons and so on. At this point it is convenient to choose a four-dimensional orthonormal basis to work with: $|e\rangle = (1, 0, 0, 0)^T$, $|g\rangle = (0, 1, 0, 0)^T$, $|c\rangle = (0, 0, 1, 0)^T$ and $|c^*\rangle = (0, 0, 0, 1)^T$. According to the matrix form of the Bloch equation Eq. (1) the first

two vectors correspond to pure excited and ground states respectively. The last two vectors, however, do not represent any real physical state and should be simply considered as convenient mathematical way to include all possible quantum paths going through superposition of the pure physical states $|e\rangle$ and $|g\rangle$, thus representing the contribution of the coherence effect. Using this notation the main equation for calculating the probability of n emission events up to time t is [23]

$$P_n(t) = (\langle e| + \langle g|)\sigma_{(t)}^{(n)} = (\langle e| + \langle g|)U_{(t,0)}^{(n)}|\sigma_{(0)}\rangle. \quad (8)$$

For example the probability of emitting zero photons is

$$P_0(t) = \sum_{i=e,g} \langle i|\mathcal{G}(t,0)|\sigma_{(0)}\rangle, \quad (9)$$

and the probability of emitting a single photon is

$$P_1(t) = \sum_{i=e,g} \langle i|\int_0^t dt_1 \mathcal{G}(t,t_1) \hat{\Gamma} \mathcal{G}(t_1,0)|\sigma_{(0)}\rangle. \quad (10)$$

Consider a laser field interacting with the molecule in the time interval (t', t) and choose a fixed point t_a inside this interval. Such a partitioning of the time axis is useful for the analysis of sequence of pulses investigated in the following section, when we distinguish between time intervals where the laser is turned on and off. First, let's split the integration over t_n in Eq. (7) into two parts:

$$U_{(t,t')}^{(n)} = \int_{t'}^t dt_n \dots = \int_{t'}^{t_a} dt_n \dots + \int_{t_a}^t dt_n \dots \quad (11)$$

Using the fact that in the first interval (t', t_a) $t_n \leq t_a$ and replacing the Green function $\mathcal{G}(t, t_n)$ by the product $\mathcal{G}(t, t_a)\mathcal{G}(t_a, t_n)$ one easily finds

$$\int_{t'}^{t_a} dt_n \dots \int_{t'}^{t_2} dt_1 \mathcal{G}(t, t_n) \hat{\Gamma} \dots \hat{\Gamma} \mathcal{G}(t_1, t') = U_{(t,t_a)}^{(0)} U_{(t_a,t')}^{(n)}. \quad (12)$$

Now, left with the integral over the second range (t_a, t) , we repeat exactly the same procedure as we did with the initial expression, but this time we split the integration over t_{n-1} into (t', t_a) and (t_a, t_n) . Similarly, using $t_{n-1} \leq t_a$ and replacing $\mathcal{G}(t_n, t_{n-1})$ by $\mathcal{G}(t_n, t_a)\mathcal{G}(t_a, t_{n-1})$ inside the first interval we find

$$\begin{aligned} \int_{t_a}^t dt_n \int_{t'}^{t_a} dt_{n-1} \dots \int_{t'}^{t_2} dt_1 \mathcal{G}(t, t_n) \hat{\Gamma} \dots \hat{\Gamma} \mathcal{G}(t_1, t') = \\ = U_{(t,t_a)}^{(1)} U_{(t_a,t')}^{(n-1)}. \end{aligned} \quad (13)$$

Repeating this algorithm n times it is easy to prove that

$$U_{(t,t')}^{(n)} = \sum_{\alpha=0}^n U_{(t,t_a)}^{(\alpha)} U_{(t_a,t')}^{(n-\alpha)}. \quad (14)$$

Eq. (14) means that the propagator corresponding to n emission events in (t', t) can be decomposed into α emission events in (t', t_a) and $n - \alpha$ emission events in (t_a, t) . The extension to more than one time point such as t_a is trivial and leads to summation over all possible permutations of the n photons propagators resulting in n emission events.

Turning back to the Eq. (8) for $P_n(t)$ and inserting the closure relation

$$\sum_{j=e,g,c,c^*} |j\rangle\langle j| = 1, \quad (15)$$

we find

$$P_n(t) = \sum_{i=e,g} \sum_{j=e,g,c,c^*} \sum_{\alpha=0}^n \langle i|U_{(t,t_a)}^{n-\alpha}|j\rangle\langle j|U_{(t_a,0)}^{\alpha}|\sigma_{(0)}\rangle \quad (16)$$

Eq. (16) describes the summation over all possible paths resulting in n emission events and suggests the following classification : the paths going through the pure states $|j\rangle = |e\rangle, |g\rangle$ may be identified as semiclassical, whereas the paths going through the states $|j\rangle = |c\rangle, |c^*\rangle$ describe the contribution of the coherence.

TWO PULSES

Now we focus on the case of two laser pulses separated by a window Δ in which the laser is turned off. The initial time is $t = 0$, the time t_1 is the moment when the first pulse is switched off. The amplitude of the external field remains equal zero $f(t) = 0$ for the delay period $t_1 < t < t_1 + \Delta$. At time $t_2 = t_1 + \Delta$ the laser is turned on again, and then again turned off for $t > t_3$ ($f(t) = 0$ for $t > t_3$). Schematically the sequence is represented in Fig. 1 for square pulses, however we emphasize that the results obtained in this section are valid for pulses of any shape. Our goal is the derivation of general expressions for $P_n(t)$ from two pulses in the limit of the long measurement time $t \rightarrow \infty$ when we know that eventually the system is in the ground state. We assume that the molecule is always in the ground state at the beginning of the experiment. If we divide the time axis into four distinct intervals : two intervals when the laser is turned on and two others when the laser is turned off, the most general expression for $U_{(t,0)}^{(n)}$ following from the extension of Eq. (14) is

$$U_{(t,0)}^{(n)} = U_{(t,t_3)}^{(n-\alpha-\beta-\gamma)} U_{(t_3,t_2)}^{(\gamma)} U_{(t_2,t_1)}^{(\beta)} U_{(t_1,0)}^{(\alpha)}, \quad (17)$$

where the superscripts α , β and γ are all non negative integer values leading to n photons (i.e. $n - \alpha - \beta - \gamma \geq 0$). The Einstein's summation rule from 0 to n must be applied to every superscript appearing twice. Inside time intervals (t, t_3) and (t_2, t_1) , when the laser is turned

off, the Rabi frequency is equal zero $\Omega = 0$, and the calculation of the Green function $\mathcal{G}(t, t')$ Eq. (5) becomes nearly trivial. For the delay interval Δ we find only two non-zero n-photon-propagators:

$$U_{(t_1+\Delta, t_1)}^{(0)} = \begin{pmatrix} e^{-\Gamma\Delta} & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & e^{(i\omega_0 - \Gamma/2)\Delta} & 0 \\ 0 & 0 & 0 & e^{-(i\omega_0 + \Gamma/2)\Delta} \end{pmatrix}, \quad (18)$$

$$U_{(t_1+\Delta, t_1)}^{(1)} = \begin{pmatrix} 0 & 0 & 0 & 0 \\ 1 - e^{-\Gamma\Delta} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix} \quad (19)$$

and $U_{(t_1+\Delta, t_1)}^{(n)} = 0$ for $n > 1$. This result is definitely expected, since if nothing excites the molecule, there is no chance to get more than a single photon. The matrix representation of the propagators in the interval ($t > t_3$) when $t \rightarrow \infty$, are found by taking the limit $\Delta \rightarrow \infty$ of Eqs. (18),(19). Now inserting the closure relation Eq. (15) between each two propagators of Eq. (17) and using the just obtained matrix elements Eqs. (18),(19) we find :

$$P_n = \lim_{t \rightarrow \infty} P_n(t) = P_n^{\text{Cla}} + e^{-\Delta \frac{\Gamma}{2}} (e^{i\Delta\omega_0} A_n^{\text{Coh}} + C.C.), \quad (20)$$

where

$$\begin{aligned} P_n^{\text{Cla}} = & \sum_{\alpha=0}^n \left\{ \langle g | U_{(t_3, t_2)}^{(n-\alpha)} | g \rangle \langle g | U_{(t_1, 0)}^{(\alpha)} | g \rangle + e^{-\Delta\Gamma} \langle g | U_{(t_3, t_2)}^{(n-\alpha)} | e \rangle \langle e | U_{(t_1, 0)}^{(\alpha)} | g \rangle \right\} + \sum_{\alpha=0}^{n-1} (1 - e^{-\Delta\Gamma}) \langle g | U_{(t_3, t_2)}^{(n-\alpha-1)} | g \rangle \langle e | U_{(t_1, 0)}^{(\alpha)} | g \rangle \\ & + \sum_{\alpha=0}^{n-1} \left\{ \langle e | U_{(t_3, t_2)}^{(n-\alpha-1)} | g \rangle \langle g | U_{(t_1, 0)}^{(\alpha)} | g \rangle + e^{-\Delta\Gamma} \langle e | U_{(t_3, t_2)}^{(n-\alpha-1)} | e \rangle \langle e | U_{(t_1, 0)}^{(\alpha)} | g \rangle \right\} + \sum_{\alpha=0}^{n-2} (1 - e^{-\Delta\Gamma}) \langle e | U_{(t_3, t_2)}^{(n-\alpha-2)} | g \rangle \langle e | U_{(t_1, 0)}^{(\alpha)} | g \rangle \end{aligned} \quad (21)$$

and

$$A_n^{\text{Coh}} = \sum_{\alpha=0}^n \langle g | U_{(t_3, t_2)}^{(n-\alpha)} | c \rangle \langle c | U_{(t_1, 0)}^{(\alpha)} | g \rangle + \sum_{\alpha=0}^{n-1} \langle e | U_{(t_3, t_2)}^{(n-\alpha-1)} | c \rangle \langle c | U_{(t_1, 0)}^{(\alpha)} | g \rangle. \quad (22)$$

Eqs. (20),(21) and (22) summarize all possible paths resulting in n photon emission events and allow simple identification of negligible terms, when particular physical constraints are taken into account. It is easy to see, that the first two terms of P_n^{Cla} Eq. (21) (those with $\sum_{\alpha=0}^n$) describe processes where all n photons are emitted during the pulses and none in the delay interval or after the second pulse. The third term of this expression represents the processes, where a single photon is emitted in the delay period (with probability $[1 - e^{-\Delta\Gamma}]$) and n-1 photons during the pulses events. Similarly, the next two terms originate from the processes, where a single photon is emitted after the second pulse and zero photons in the delay interval, and finally, the last term describes situations, where one photon is emitted in the delay interval and another after the second pulse. This interpretation may be used to simplify the calculations, as for instance in the case of the short pulses considered below, where we neglect the trajectories with photons emitted during the

pulse events.

Although Eqs. (20),(21) and (22) are very general, they already contain interesting physical information. First of all, we pay attention to the fact, that the coherence terms A_n^{Coh} , describing the processes where the molecule is left in the superposition of the pure states at the end of the first pulse (i.e. the paths going through the states $|c\rangle$ and $|c^*\rangle$), never include trajectories where a photon is emitted within the delay interval Δ . Mathematically this follows from Eqs. (18) and (19), and physically it makes sense, because spontaneous collapse into the ground state destroys the coherence. Secondly, we see, that the coherence terms are multiplied by the exponentially decaying factor $e^{-\Gamma\Delta/2}$, responsible for the dephasing effect, and oscillate in Δ with orbital frequency ω_0 (see the $e^{i\Delta\omega_0}$ term in Eq. (20)). In optics ω_0 is much larger than the inverse of τ - the minimum time resolution of the measurement device : $\tau\omega_0 \gg 1$. Therefore, in order to match our results

for the probability of emitting n photons to those observed by an experimentalist, it is essential to treat the coherence terms as stochastic variables - i.e. it is reasonable to replace them with their time average, which is equal zero. However, it should not be forgotten that : (i) in the limit $\Delta \rightarrow 0$, when the pulses are attached together, the coherence contribution A_n^{Coh} becomes non-oscillating and non-negligible part of P_n , and (ii) in non-optical microwave experiments, where the absorption frequency is comparable with the time resolution of the measurement device [8], the influence of the coherence trajectories is important.

It is possible to derive another useful expression for the probability of emitting n photons from two pulses. First

we note, that according to Eqs. (8), (18) and (19) the probability of emitting n photons from any single pulse or sequence of pulses of total length T in the limit of infinitely long measurement time $t \rightarrow \infty$ is

$$P_n = \langle g|U_{(T,0)}^{(n)}|g\rangle + \langle e|U_{(T,0)}^{(n-1)}|g\rangle, \quad (23)$$

(where for $n=0$ the second term $\langle e|U_{(T,0)}^{(-1)}|g\rangle = 0$). From the physical point of view the second term of Eq. (23) expresses the fact, that the molecule left in the pure excited state eventually decays to the ground state by spontaneous photon emission. Simple rearrangement of Eqs. (21) and (22), with details given in Appendix A, results in :

$$P_n = \sum_{\alpha=0}^n P_{n-\alpha}^{I_2} P_{\alpha}^{I_1} + e^{-\Delta\Gamma} \left\{ P_n^{I_2 I_1} - \sum_{\alpha=0}^n P_{n-\alpha}^{I_2} P_{\alpha}^{I_1} + \left[(e^{\Delta(\Gamma/2+i\omega_0)} - 1) A_n^{\text{Coh}} + C.C. \right] \right\}. \quad (24)$$

Here $P_n^{I_1} = \langle g|U_{(t_1,0)}^{(n)}|g\rangle + \langle e|U_{(t_1,0)}^{(n-1)}|g\rangle$ is the probability of emitting n photons only from the first pulse [24, 25], similarly $P_n^{I_2} = \langle g|U_{(t_3,t_2)}^{(n)}|g\rangle + \langle e|U_{(t_3,t_2)}^{(n-1)}|g\rangle$ designates the probability of emitting n photons only from the second pulse, and

$$P_n^{I_2 I_1} = \sum_{\alpha=0}^n \langle g|U_{(t_3,t_2)}^{(n-\alpha)} U_{(t_1,0)}^{(\alpha)}|g\rangle + \sum_{\alpha=0}^{n-1} \langle e|U_{(t_3,t_2)}^{(n-1-\alpha)} U_{(t_1,0)}^{(\alpha)}|g\rangle \quad (25)$$

is the probability of emitting n photons from the two pulses produced one immediately after another (i.e. with zero delay). This formulation of P_n Eq. (24) shows, that the first term $\sum_{\alpha=0}^n P_{n-\alpha}^{I_2} P_{\alpha}^{I_1}$ represents the sum of all possible ways of emitting n photons from the both pulses, as if the consequences of the interaction of the molecule with the first pulse had no influence on the state of the system at the beginning of the second pulse, i.e. like if the treatment of each pulse could be done independently. Nevertheless, since such an influence exists, it is reasonable to define the rest of the terms on the righthand side of Eq. (24) as a correlation:

$$C(\Delta) = P_n - \sum_{\alpha=0}^n P_{n-\alpha}^{I_2} P_{\alpha}^{I_1} = e^{-\Delta\Gamma} \left\{ P_n^{I_2 I_1} - \sum_{\alpha=0}^n P_{n-\alpha}^{I_2} P_{\alpha}^{I_1} + \left[(e^{\Delta(\Gamma/2+i\omega_0)} - 1) A_n^{\text{Coh}} + C.C. \right] \right\}. \quad (26)$$

Note that Eq. (24) makes perfect physical sense in the limits $\Delta \rightarrow \infty$ and $\Delta \rightarrow 0$ where we find trivially expected results. In the first case only the first term on the

righthand side of Eq. (24) survives - i.e. this limit describes the situation where the interaction of the molecule with the first pulse indeed has no influence on the interaction of the molecule with the second pulse, since all coherence effects have enough time to decay completely. And the second limit gives $P_n = P_n^{I_2 I_1}$. We emphasize, that in the first case, once the probabilities of emitting n photons from each single pulse are known, the efforts needed for the calculations are considerably reduced. However, care must be taken while using Eq. (24) for the calculation of the second limit $\Delta \rightarrow 0$, since the continuity of the laser's phase plays important role, as demonstrated on the example of two square pulses in the subsequent section.

EXAMPLE : TWO SQUARE PULSES

In this section we apply our general results to the concrete example of two identical square laser pulses. Consider the sequence :

$$f(t) = \begin{cases} \cos(\omega_L t + \phi_1) & 0 < t < t_1 \\ 0 & t_1 < t < t_2 \\ \cos[\omega_L(t - t_2) + \phi_2] & t_2 < t < t_3 \\ 0 & t_3 < t \end{cases} \quad (27)$$

where $t_1 = t_3 - t_2 = T$ - is the pulse's duration, $t_2 - t_1 = \Delta$ - is the delay period between the pulses and ϕ_1 and ϕ_2 are the initial phases of each pulse. For simplicity we assume, that the laser frequency $\omega_L = \omega_0$, namely we consider the case of zero detuning, and also the initial phase of the first pulse is zero $\phi_1 = 0$. The time dependence

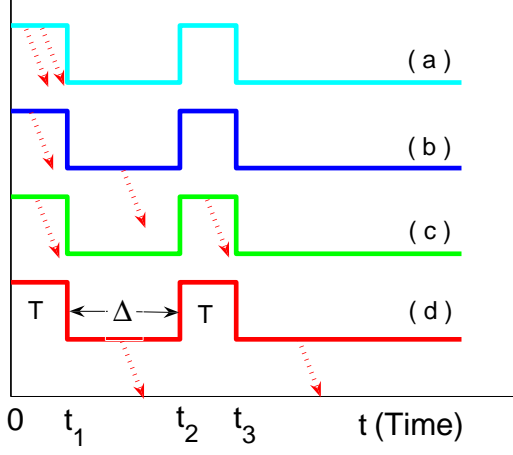


FIG. 1: Two square laser pulses as modeled in Eq. (27). T is the length of a single pulse and Δ is the delay interval between the pulses. The dashed arrows show four cases out of eight possibilities of emission of two photons. For example: (a) two photons are emitted within the duration of the first pulse.

of the Rabi frequency Ω , describing the interaction, is schematically illustrated in Fig. 1. The propagators acting on the molecule during the square pulses are found using the Rotating Wave Approximation (RWA). In Appendixes B and C we show, that within RWA Eq. (20) can be rewritten in the form

$$P_n = p_n^{\text{Cla}} + e^{-\frac{\Gamma}{2}} (e^{i(\Delta+T)\omega_0 - \phi_2} a_n^{\text{Coh}} + C.C.), \quad (28)$$

where the definition of p_n^{Cla} and a_n^{Coh} follows from P_n^{Cla}

and A_n^{Coh} Eqs. (21),(22) by replacing all n-photon-propagators Eq. (7) by $\tilde{U}_{(t,t')}^{(n)}$ - the n-photon-propagators calculated within RWA (see the derivation of Eq. (71) in Appendix B). All mathematical manipulations and calculations were obtained with the help of Mathematica 5.0.

First we consider in detail the probability of emitting zero photons. For the calculation of $P_0(t)$ we need the zero photon propagator. This is the simplest case, since there is only one possible permutation. According to Eq. (17) we have :

$$U_{(t,0)}^{(0)} = U_{(t,t_3)}^{(0)} U_{(t_3,t_2)}^{(0)} U_{(t_2,t_1)}^{(0)} U_{(t_1,0)}^{(0)}. \quad (29)$$

Inserting the closure relation Eq. (15) and applying RWA lead to :

$$p_0^{\text{Cla}} = e^{-\Gamma\Delta} \langle g | \tilde{U}_{(t_3,t_2)}^{(0)} | e \rangle \langle e | \tilde{U}_{(t_1,0)}^{(0)} | g \rangle + \langle g | \tilde{U}_{(t_3,t_2)}^{(0)} | g \rangle \langle g | \tilde{U}_{(t_1,0)}^{(0)} | g \rangle, \quad (30)$$

$$a_0^{\text{Coh}} = \langle g | \tilde{U}_{(t_3,t_2)}^{(0)} | c \rangle \langle c | \tilde{U}_{(t_1,0)}^{(0)} | g \rangle, \quad (31)$$

Calculating the matrix elements of Eqs. (30) and (31) we find the following explicit expression for $P_0 = \lim_{t \rightarrow \infty} P_0(t)$:

$$P_0 = \frac{16\Omega^4 e^{-T-\Delta}}{(1-4\Omega^2)^2} \sinh^4 \left(\frac{\sqrt{1-4\Omega^2}}{4} T \right) + \frac{e^{-T}}{(1-4\Omega^2)^2} \left[(1-2\Omega^2) \cosh \left(\frac{\sqrt{1-4\Omega^2}}{2} T \right) + \sqrt{1-4\Omega^2} \sinh \left(\frac{\sqrt{1-4\Omega^2}}{2} T \right) - 2\Omega^2 \right]^2 - \frac{8\Omega^2}{(1-4\Omega^2)^2} e^{-T-\Delta/2} \sinh^2 \left(\frac{\sqrt{1-4\Omega^2}}{4} T \right) \left[\sqrt{1-4\Omega^2} \cosh \left(\frac{\sqrt{1-4\Omega^2}}{4} T \right) + \sinh \left(\frac{\sqrt{1-4\Omega^2}}{4} T \right) \right]^2 \cos[\omega_0 (\Delta + T) - \phi_2], \quad (32)$$

where we set $\Gamma = 1$ for simplicity. The last term, exhibiting oscillations due to the $\cos[\omega_0 (\Delta + T) - \phi_2]$, results from the quantum paths going through the $|c\rangle$ and $|c^*\rangle$, thus representing the coherence effect. Of course, when $T = 0$ or $\Omega = 0$, $P_0 = 1$ since no photons are emitted, and if $T \rightarrow \infty$, $P_0 = 0$ since many photons are emitted. Similar calculations were made also for P_1 and P_2 - see Eqs. (81), (88) for the final results in Appendix C.

For very intense laser fields, when the Rabi frequency is much larger than the inverse life time of the excited state,

taking the limit $\Omega \gg 1$ of Eq. (32) we obtain :

$$\lim_{\Omega \gg 1} P_0 \sim e^{-T} \left\{ e^{-\Delta} \sin^4 \left(\frac{\Omega T}{2} \right) + \cos^4 \left(\frac{\Omega T}{2} \right) - \frac{1}{2} e^{-\Delta/2} \sin^2(\Omega T) \cos[\omega_0(\Delta + T) - \phi_2] \right\}. \quad (33)$$

And using Eqs. (81), (88):

$$\begin{aligned} \lim_{\Omega \gg 1} P_1 = \frac{e^{-T}}{8} & \left\{ 4 \sin^2(\Omega T) + 2T \left[1 - \sin^2 \left(\frac{\Omega T}{2} \right) (1 - e^{-\Delta}) \right] + T \sin^2(\Omega T) (1 + e^{-\Delta}) \right\} \\ & + \frac{e^{-(T+\Delta/2)}}{4} (T+2) \sin^2(\Omega T) \cos[\omega_0(\Delta + T) - \phi_2], \end{aligned} \quad (34)$$

$$\begin{aligned} \lim_{\Omega \gg 1} P_2 = e^{-T} & \left\{ \left[\sin^4 \left(\frac{\Omega T}{2} \right) + \frac{T^2}{64} \cos(\Omega T) \right] (1 - e^{-\Delta}) + \frac{T}{4} [\cos^2(\Omega T) + 2] \right\} \\ & + \frac{e^{-T}}{32} T^2 (\cos^2(\Omega T) + 4) (1 + e^{-\Delta}) - \frac{e^{-(T+\Delta/2)}}{16} T(T+4) \sin^2(\Omega T) \cos[\omega_0(\Delta + T) - \phi_2]. \end{aligned} \quad (35)$$

Finally, we would like to investigate the limiting behavior of P_0 , P_1 and P_2 within the strong fields approximation in the case of long $\Delta \rightarrow \infty$ and short $\Delta \rightarrow 0$ delay intervals. As shown in [24, 25], the probabilities of emission 0, 1 and 2 photons from a single square pulse of length T (see Eq. (23)) are given by

$$\lim_{\Omega \gg 1} P_0^I = \lim_{\Omega \gg 1} P_0^{I_1} = \lim_{\Omega \gg 1} P_0^{I_2} \sim e^{-T/2} \cos^2 \left(\frac{\Omega T}{2} \right), \quad (36)$$

$$\lim_{\Omega \gg 1} P_1^I \sim \frac{e^{-T/2}}{8} [4 + 2T - (4 + T) \cos(\Omega T)] \quad (37)$$

and

$$\lim_{\Omega \gg 1} P_2^I \sim \frac{e^{-T/2}}{64} T [4T + 16 + (8 + T) \cos(\Omega T)]. \quad (38)$$

Taking the limit $\Delta \gg 1$ of Eq. (32) we find

$$\lim_{\Omega \gg 1, \Delta \gg 1} P_0 = (P_0^I)^2 \sim e^{-T} \cos^4 \left(\frac{\Omega T}{2} \right), \quad (39)$$

which is equal precisely to the product of the probabilities of emitting zero photons from two single square pulses Eq. (36) and completely agrees with Eq. (24). Now using Eqs. (24), (37), (38) and the fact, that the two pulses are identical, we can easily obtain the limit $\Delta \rightarrow \infty$ of P_1 and P_2 :

$$\begin{aligned} \lim_{\Omega \gg 1, \Delta \gg 1} P_1 &= 2P_1^I P_0^I = \\ & \frac{e^{-T}}{4} \left[(8 + 3T) \cos^2 \left(\frac{\Omega T}{2} \right) - 2(4 + T) \cos^4 \left(\frac{\Omega T}{2} \right) \right] \end{aligned} \quad (40)$$

and

$$\begin{aligned} \lim_{\Omega \gg 1, \Delta \gg 1} P_2 &= 2P_0^I P_2^I + (P_1^I)^2 = \frac{e^{-T}}{64} [24 + T(40 + 9T) + \\ & (-32 + T^2) \cos(\Omega T) + (8 + T(8 + T)) \cos(2\Omega T)]. \end{aligned} \quad (41)$$

Considering the opposite limit $\Delta \rightarrow 0$ we remind, that the contribution of the coherence paths going through the states $|c\rangle$ and $|c^*\rangle$ must not be neglected. Moreover, it is essential to take into account, that two attached square pulses of the same Rabi frequency are equal to a single long square pulse, only if $\phi_2 = \phi_1 + \omega_0(\Delta + T)$ - i.e. the pulse is continuous. Assuming for simplicity, that this is the case, when $\Delta \rightarrow 0$ from Eq. (32) we find for P_0 :

$$\lim_{\Omega \gg 1, \Delta \ll 1} P_0 \sim e^{-T} \cos^2(\Omega T), \quad (42)$$

which once again agrees with Eq. (24), since it is exactly the result of replacing T with 2T in Eq. (36). Similarly the limits $\Delta \rightarrow 0$ of P_1 and P_2 may be obtained by replacing T with 2T in Eqs. (37) and (38).

In Fig. 2, neglecting the fast oscillating coherence paths, we plotted the semiclassical terms p_0^{Cla} , p_1^{Cla} and p_2^{Cla} for the relatively long $\Delta = 3$ and short $\Delta = 0.5$ delay intervals for the case of strong laser field $\Omega = 10$. Comparing the graphs one may see, that the dependence of p_1^{Cla} on Δ is visibly weaker than those of p_0^{Cla} and p_2^{Cla} (we explain this effect later - see the discussion below Table 1). When $\Gamma T \gg 1$, we expect that : (i) p_0^{Cla} , p_1^{Cla} and

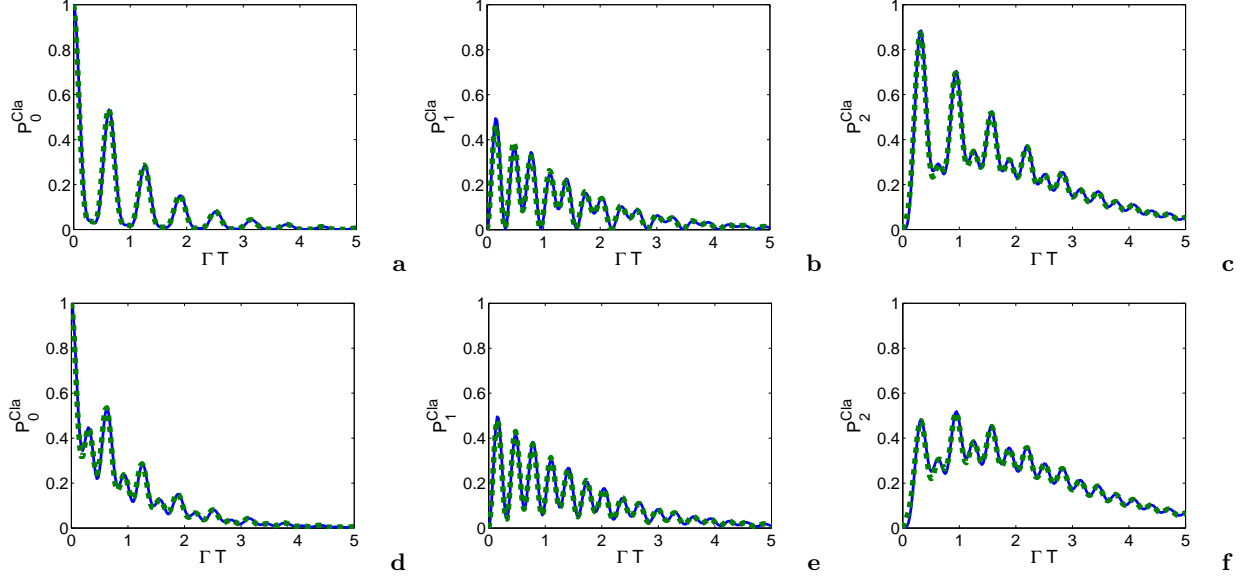


FIG. 2: The semiclassical parts of probabilities of zero, one and two (from left to right) photon emissions from the two laser pulses as a function of T - the duration of a pulse with $\Omega = 10\Gamma$. The solid line is the exact result Eqs. (32), (81) and (88) and the dashed curve show the approximation in the limit of strong fields Eqs. (33), (34) and (35). The upper row (a, b, c) illustrates the result for $\Delta = 3$ and the lower row (e, f, d) illustrates the same probabilities for $\Delta = 0.5$.

p_2^{Cla} are all small, since many photons are expected to be emitted during the pulses, and (ii) independent of Δ , since the contribution of the photons emitted during the pulse event is much larger than the contribution of the photons emitted in the delay interval. Such a behavior

is clearly seen for p_2^{Cla} (compare Figs. 2.c and 2.f) where the difference between the case $\Delta = 3$ and $\Delta = 0.5$ is stronger for short T . Below we prove this in a Poissonian limit.

Strong and Short Pulses

The sequence of two very short and strong pulses is important due to its numerous practical applications. Mathematically we define this limit as $T \rightarrow 0$, $\Omega \rightarrow \infty$ in such a way, that the product ΩT stays of the order of unity $\Omega T \sim 1$ (automatically leading also to $\Omega \gg \Gamma$), otherwise the molecule will never reach the excited state, and the probability to obtain non-zero results for P_1 and P_2 will be negligible. As a consequence, the spontaneous emission process during the pulse event may be neglected, and therefore, it is reasonable to approximate the behavior of the system by simple Shrödinger evolution with well-known Rabi oscillations. In this limit the photons can be emitted only in the delay interval or after the second pulse, while the only non-zero propagator acting on the molecule during the pulses within RWA has the

following matrix representation :

$$\lim_{\substack{T \rightarrow 0, \\ \Omega \rightarrow \infty}} \tilde{U}_{(T,0)}^{(0)} = \begin{pmatrix} \cos^2 \frac{\Omega T}{2} & \sin^2 \frac{\Omega T}{2} & -i \frac{\sin \Omega T}{2} & i \frac{\sin \Omega T}{2} \\ \sin^2 \frac{\Omega T}{2} & \cos^2 \frac{\Omega T}{2} & i \frac{\sin \Omega T}{2} & -i \frac{\sin \Omega T}{2} \\ -i \frac{\sin \Omega T}{2} & i \frac{\sin \Omega T}{2} & \cos^2 \frac{\Omega T}{2} & \sin^2 \frac{\Omega T}{2} \\ i \frac{\sin \Omega T}{2} & -i \frac{\sin \Omega T}{2} & \sin^2 \frac{\Omega T}{2} & \cos^2 \frac{\Omega T}{2} \end{pmatrix}, \quad (43)$$

which is independent of Γ . Note, that since this zero-photon-propagator Eq. (43) describes the conservative evolution of the system, the transformation is unitary, all the elements exhibit Rabi oscillations, and symmetry and reversibility of the matrix elements are found: $\langle e | \tilde{U}_{(T,0)}^{(0)} | e \rangle = \langle g | \tilde{U}_{(T,0)}^{(0)} | g \rangle$, $\langle e | \tilde{U}_{(T,0)}^{(0)} | g \rangle = \langle g | \tilde{U}_{(T,0)}^{(0)} | e \rangle$ etc.

Now we consider P_0 , P_1 and P_2 in the limit of the short and strong pulses and demonstrate how this physical constrain can help in reducing the number of paths appearing in Eqs. (20),(21),(22). The exact expressions for $U_{(t,0)}^{(1)}$ and $U_{(t,0)}^{(2)}$, according to Eq. (17) consist of the

sum of 4 and 10 terms respectively - see Eqs. (78), (86) in Appendix C. After neglecting the trajectories where photons are emitted within the pulse events (since $T \rightarrow 0$) we have :

$$\begin{aligned} \lim_{T \rightarrow 0, \Omega \rightarrow \infty} U_{(t,0)}^{(1)} &= U_{(t,t_3)}^{(1)} U_{(t_3,t_2)}^{(0)} U_{(t_2,t_1)}^{(0)} U_{(t_1,0)}^{(0)} \\ &+ U_{(t,t_3)}^{(0)} U_{(t_3,t_2)}^{(0)} U_{(t_2,t_1)}^{(1)} U_{(t_1,0)}^{(0)} \end{aligned} \quad (44)$$

and

$$\lim_{T \rightarrow 0, \Omega \rightarrow \infty} U_{(t,0)}^{(2)} = U_{(t,t_3)}^{(1)} U_{(t_3,t_2)}^{(0)} U_{(t_2,t_1)}^{(1)} U_{(t_1,0)}^{(0)}. \quad (45)$$

This is one example where the formulation of photon statistics based on quantum trajectories is very convenient, since we can identify the underlying physical processes and make approximations. Inserting the closure relation Eq. (15) between every two propagators of Eqs. (44), (45) and using the matrix elements of the zero-photon-propagator Eq. (43), we obtain the leading semiclassical and coherence terms of P_0 , P_1 and P_2 in the limit of the short and strong pulses. The results are summarized in Table 1 below and they are valid for any sequence of short pulses.

n	p_n^{Cla}	a_n^{Coh}
0	$\langle g \tilde{U}_{(t_3,t_2)}^{(0)} g \rangle \langle g \tilde{U}_{(t_1,0)}^{(0)} g \rangle + e^{-\Gamma\Delta} \langle g \tilde{U}_{(t_3,t_2)}^{(0)} e \rangle \langle e \tilde{U}_{(t_1,0)}^{(0)} g \rangle$	$\langle g \tilde{U}_{(t_3,t_2)}^{(0)} c \rangle \langle c \tilde{U}_{(t_1,0)}^{(0)} g \rangle$
1	$\langle g \tilde{U}_{(t_3,t_2)}^{(0)} g \rangle \langle e \tilde{U}_{(t_1,0)}^{(0)} g \rangle + \langle e \tilde{U}_{(t_3,t_2)}^{(0)} g \rangle \langle g \tilde{U}_{(t_1,0)}^{(0)} g \rangle$	$\langle e \tilde{U}_{(t_3,t_2)}^{(0)} c \rangle \langle c \tilde{U}_{(t_1,0)}^{(0)} g \rangle$
2	$\langle e \tilde{U}_{(t_3,t_2)}^{(0)} g \rangle \langle e \tilde{U}_{(t_1,0)}^{(0)} g \rangle (1 - e^{-\Gamma\Delta})$	0

Table 1: Photon statistics for short pulses.

Note, that the coherence terms of P_2 vanish, since emission of a photon in the delay interval, necessary for emitting two photons in the limit of very short pulses, destroys the coherence. Using the symmetry and reversibility of the zero-photon-propagator matrix elements Eq. (43), it is easy to show that $a_0^{\text{Coh}} = -a_1^{\text{Coh}}$ and $p_0^{\text{Cla}} + p_1^{\text{Cla}} + p_2^{\text{Cla}} = 1$, i.e. the semiclassical paths conserve probability. Finally, we bring attention to the fact, that the semiclassical paths of P_1 do not depend neither on the spontaneous emission rate Γ nor on the delay interval duration Δ (see Fig. 2.b and Fig. 2.e). Comparing the two non-negligible trajectories of p_1^{Cla} with Eq. (24), we see that they correspond to the first term of the righthand side of this equation - i.e to the product of probabilities of emitting 0 and 1 photons, related to each one of the pulses independently.

Using the matrix elements Eq. (43) and Table 1, after some algebra we obtain explicitly :

$$\lim_{T \rightarrow 0, \Omega \rightarrow \infty} P_0 = e^{-\Delta} \sin^4 \left(\frac{\Omega T}{2} \right) + \cos^4 \left(\frac{\Omega T}{2} \right) - \frac{1}{2} e^{-\Delta/2} \sin^2(\Omega T) \cos[\omega_0(T + \Delta) - \phi_2] \quad (46)$$

which is the $\Omega \rightarrow \infty$, $T \rightarrow 0$ limit of Eq. (32).

$$\lim_{T \rightarrow 0, \Omega \rightarrow \infty} P_1 = \frac{1}{2} \sin^2(\Omega T) \left\{ 1 + e^{-\Delta/2} \cos[\omega_0(T + \Delta) - \phi_2] \right\} \quad (47)$$

and

$$\lim_{T \rightarrow 0, \Omega \rightarrow \infty} P_2 = (1 - e^{-\Delta}) \sin^4 \left(\frac{\Omega T}{2} \right) \quad (48)$$

It is easy to see, that when $T \rightarrow 0$ the Eqs. (34), (35) reduce to Eqs. (47), (48) as expected.

For a π -pulse defined by $\Omega T = \pi + 2\pi n$ [24, 25], where n is a non negative integer, in the strong field limit we obtain :

$$\lim_{T \rightarrow 0, \Omega \rightarrow \infty} P_0 \sim e^{-\Delta}. \quad (49)$$

This behavior may be easily understood for : substituting

$\Omega T = \pi$ into Eq. (43) we have

$$\lim_{\substack{T \rightarrow 0, \Omega \rightarrow \infty, \\ \Omega T = \pi}} \tilde{U}_{(T,0)}^{(0)} = \begin{pmatrix} 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{pmatrix} \quad (50)$$

The physical meaning of this propagator follows directly from its matrix representation : as well-known, the ideal π -pulse simply switches the state of the molecule from the excited to the ground state and vice versa. Thus, the first π -pulse of the sequence pumps the molecule from the ground state to the excited state. If the delay between the pulses Δ is long, the molecule will emit a photon before the arrival of the second pulse, and then $\lim_{T \rightarrow 0, \Omega \rightarrow \infty} P_0 = 0$. Contrary, if $\Delta \ll 1$, the second π -pulse pushes the molecule back to the ground state before the emission of a photon, and then $\lim_{T \rightarrow 0, \Omega \rightarrow \infty} P_0 = 1$. We also notice, that the interference $\cos[\omega_0(T + \Delta) - \phi_2]$ term vanishes for the π -pulses, since according to Eq. (50) the off-diagonal matrix elements giving raise to this term are equal zero. On the opposite, for a $\pi/2$ -pulse, defined by $\Omega T = \pi/2 + 2\pi n$, the influence of the coherence on the photon statistics generally does not vanish:

$$\lim_{\Omega \gg 1} P_0 \sim \frac{1}{4} \left\{ e^{-\Delta} + 1 - 2e^{-\Delta/2} \cos[\omega_0(\Delta + T)] \right\} \quad (51)$$

Once again we remind, that in optics in many cases the ideal π and $\pi/2$ -pulses are considered where the interaction time $\Gamma T \rightarrow 0$, and then $e^{-T} = 1$, but $\omega_0 T$ is not a small number, especially because we work under the assumption $\Omega \ll \omega_0$, which is essential for the two level model approximation of the molecule and for the assumption, that the spontaneous emission rate Γ is not effected by the presence of the laser field [21].

Weak and Long Pulses

Here we consider the case of very long and weak pulses. In this limit the delay interval has a negligible effect on P_n . In this limit we expect, that according to Eq. (24) the probability of emitting n photons from two separated pulses may be approximated by $P_n^{I_2 I_1}$ - the probability of emitting n photons from two attached pulses with zero delay :

$$\lim_{T \rightarrow \infty} P_n = P_n^{I_2 I_1} = \sum_{\alpha=0}^n \langle g | U_{(2T)}^{(\alpha)} | g \rangle + \sum_{\alpha=0}^{n-1} \langle e | U_{(2T)}^{(\alpha)} | g \rangle \quad (52)$$

Taking the limit $\Omega \rightarrow 0$, $T \rightarrow \infty$ in such a way that $\Omega^2 T$ remains finite of the exact solution for P_0 , P_1 and

P_2 Eqs. (32),(81),(88), we find

$$\lim_{\Omega \rightarrow 0, T \rightarrow \infty} P_0 = e^{-2\Omega^2 T} \quad (53)$$

$$\lim_{\Omega \rightarrow 0, T \rightarrow \infty} P_1 = 2\Omega^2 T e^{-2\Omega^2 T} \quad (54)$$

$$\lim_{\Omega \rightarrow 0, T \rightarrow \infty} P_2 = \frac{(2\Omega^2 T)^2}{2!} e^{-2\Omega^2 T} \quad (55)$$

$$\lim_{\Omega \rightarrow 0, T \rightarrow \infty} P_n = \frac{(2\Omega^2 T)^n}{n!} e^{-2\Omega^2 T} \quad (56)$$

Indeed one can show, that Eq. (52) and the limiting behavior Eqs.(53-56) of the exact results are identical. Note, that Eq. (56) corresponds to Poissonian statistics. This behavior originates from the fact, that because of the long pulses duration and weak laser field, the leading terms of P_n are those, where photon emissions are well separated one from another on the time axis, and therefore photon statistics is described by nearly uncorrelated emission events.

The upper and lower bounds for strong pulses

Finally we investigate the upper and lower bounds of P_0 , P_1 and P_2 within the strong field approximation. Calculating the first and the second order partial derivatives with respect to T , we find the extremum of Eqs. (33), (34) and (35), and neglecting the ultra-fast oscillating coherence terms, obtain the bounds of semiclassical parts of P_0 , P_1 and P_2 :

$$e^{-(T+\Delta)} \leq p_0^{\text{Cla}} \leq e^{-T}, \quad (57)$$

$$\frac{1}{4} T e^{-(T+\Delta)} \leq p_1^{\text{Cla}} \leq \frac{e^{-T}}{8} [4 + 3T(1 + e^{-\Delta})], \quad (58)$$

$$\frac{3}{4} T e^{-T} \leq p_2^{\text{Cla}} \leq e^{-T} \left(1 - e^{-\Delta} + \frac{3}{4} T \right). \quad (59)$$

where once again $\Gamma = 1$.

The origin of Eqs. (57),(58) and (59), although non-trivial for a finite T , can be easily understood in the limit of the short pulses $T \rightarrow 0$. The upper bound of p_0^{Cla} is obvious, since if the interaction time is zero, no photons will be emitted for sure. Further, since we neglect the probability of emitting photons during the pulses, p_0^{Cla} may only be decreased by the probability of not emitting a photon during the delay interval - $e^{-\Delta}$. Considering p_1^{Cla} we see, that Eq. (47) reaches the maximum value

$-\frac{1}{2}$, when $\Omega T = \pi/2$. Hence, the maximization of p_1^{Cla} corresponding to the interaction with a sequence of two pulses is achieved by applying two ideal $\pi/2$ -pulses. Finally, from Eq. (48) for $\lim_{T \rightarrow 0, \Omega \rightarrow \infty} P_2$ follows, that maximum of this expression is found for $\Omega T = \pi$, and hence the optimization of P_2 is achieved by two ideal π -pulses.

Learning from this simple example, although not rigorously, we extend it to the conclusion, that the maximum of P_n ($n > 1$) for any fixed interaction time is optimized by producing n equally separated π -pulses. This statement follows from the following argument : as far as we work under assumption, that the laser field does not effect the spontaneous emission process, the maximization of P_n in any limited time interval may be achieved by minimization of induced emission, which is guaranteed by the strong and short ideal π -pulses better than any by any others.

In Fig. 3 we show the maximum of p_2^{Cla} from a sequence of two equal square pulses as a function of the interaction's strength Ω and pulse's duration T for three fixed values of the total interaction time $2T + \Delta$. The curves were obtained using the extremum conditions of the exact expression for P_2 Eq. (88). From Fig. 3 we see, that as the interaction time ΓT becomes shorter, the delay period Δ longer and the Rabi frequency Ω larger, the probability of emitting 2 photons is getting close to 1. Although it becomes equal exactly 1 only for two ideal π -pulses separated by infinite delay, the graph shows, that starting from some range of parameters the increasing of p_2^{Cla} slows down, so that further increasing Ω does not contribute much. Finally, we note that for short delay intervals $\Delta < 1$ the maximum of p_2^{Cla} is much less than 1 as expected.

SUMMARY

We obtained general expressions for the probability of n photon emission events for a two level system interacting with two laser pulses separated by a delay interval Δ . The photon statistic was represented as summation over quantum trajectories, which allowed simple intuitive physical interpretation of the final results Eqs. (20), (21), (22). In particular, the contribution of the coherence effect, resulting from the quantum trajectories going through the superposition of the pure states at the end of the first pulse, was discussed. Although in optics it might be difficult to detect this effect experimentally, since the coherence paths oscillate in Δ with extremely large molecule absorption frequency ω_0 , nevertheless in microwave spectroscopy, dealing with lower range of absorption frequencies, the coherence effect is important

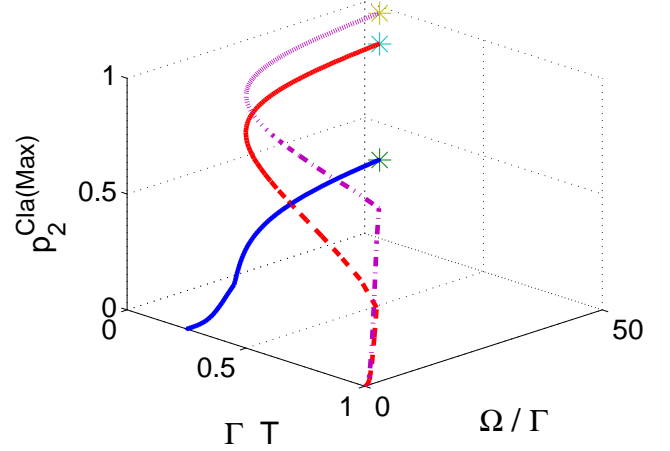


FIG. 3: The maximum of the probability of emission of two photons in a two-pulse laser field. The t_3 of the end time of second pulse is fixed at 0.5 (solid curve), 2.0 (dashed curve), 4.5 (dot-dashed curve), respectively. The delay time between two pulses, $\Delta = t_3 - 2T$. The star gives the asymptotic behavior of Eq. (88) in the limit of strong fields ($\Omega = 50$) and short pulse with $\Omega T = \pi$, $\Gamma = 1$.

[8]. In addition, the correlation function $C(\Delta)$ Eq. (26) was suggested as a measure of the photon statistics deviation from a treatment where the sequence of pulses is considered as if the pulses were independent. This correlation might be a useful tool to quantify the coherence and “memory” of single molecules, atoms or quantum dots through the measured photon statistics.

The application of our general results was demonstrated on detailed calculation of P_0 , P_1 and P_2 - the probabilities of emitting 0, 1 and 2 photons from the sequence of two square laser pulses Eqs. (32), (81) and (88) in the limit of long measurement times $t \rightarrow \infty$. The physical interpretation of the quantum paths was shown to be useful in reducing the complexity of calculations in the limit of short and strong pulses (e.g. neglecting the paths where the photons are emitted within the pulse events). Finally, the non-trivial upper and lower bounds for the strong square pulses with finite duration were obtained. This kind of information is useful in experiments, where pulses are neither infinitely short not infinitely strong. Our approach can be applied to the theoretical study of other types of non-linear spectroscopy such as three level systems, systems undergoing stochastic dynamics [3], or Josephson junction qubits [8] controlled by microwave radiation, where the strong dependence on the contribution of coherence was already experimentally proved.

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APPENDIX A

In this appendix we give the detailed derivation of Eq. (24). Consider the semiclassical trajectories Eq. (21) of P_n from the two pulses. First let us sort the terms according to

$$\begin{aligned}
P_n^{\text{Cla}} = & \sum_{\alpha=0}^n \langle g|U_{(t_3,t_2)}^{(n-\alpha)}|g\rangle \langle g|U_{(t_1,0)}^{(\alpha)}|g\rangle + \sum_{\alpha=0}^{n-1} \langle e|U_{(t_3,t_2)}^{(n-\alpha-1)}|g\rangle \langle g|U_{(t_1,0)}^{(\alpha)}|g\rangle + \sum_{\alpha=0}^{n-1} \langle g|U_{(t_3,t_2)}^{(n-\alpha-1)}|g\rangle \langle e|U_{(t_1,0)}^{(\alpha)}|g\rangle \\
& + \sum_{\alpha=0}^{n-2} \langle e|U_{(t_3,t_2)}^{(n-\alpha-2)}|g\rangle \langle e|U_{(t_1,0)}^{(\alpha)}|g\rangle + e^{-\Delta\Gamma} \left\{ \sum_{\alpha=0}^n \langle g|U_{(t_3,t_2)}^{(n-\alpha)}|e\rangle \langle e|U_{(t_1,0)}^{(\alpha)}|g\rangle + \sum_{\alpha=0}^{n-1} \langle e|U_{(t_3,t_2)}^{(n-\alpha-1)}|e\rangle \langle e|U_{(t_1,0)}^{(\alpha)}|g\rangle \right. \\
& \left. - \sum_{\alpha=0}^{n-1} \langle g|U_{(t_3,t_2)}^{(n-\alpha-1)}|g\rangle \langle e|U_{(t_1,0)}^{(\alpha)}|g\rangle - \sum_{\alpha=0}^{n-2} \langle e|U_{(t_3,t_2)}^{(n-\alpha-2)}|g\rangle \langle e|U_{(t_1,0)}^{(\alpha)}|g\rangle \right\} \quad (60)
\end{aligned}$$

Now we consider the sum of the first two terms

$$\begin{aligned}
& \sum_{\alpha=0}^n \langle g|U_{(t_3,t_2)}^{(n-\alpha)}|g\rangle \langle g|U_{(t_1,0)}^{(\alpha)}|g\rangle + \sum_{\alpha=0}^{n-1} \langle e|U_{(t_3,t_2)}^{(n-\alpha-1)}|g\rangle \langle g|U_{(t_1,0)}^{(\alpha)}|g\rangle \\
& = \left\{ \langle g|U_{(t_3,t_2)}^{(n)}|g\rangle + \langle e|U_{(t_3,t_2)}^{(n-1)}|g\rangle \right\} \langle g|U_{(t_1,0)}^{(0)}|g\rangle + \left\{ \langle g|U_{(t_3,t_2)}^{(n-1)}|g\rangle + \langle e|U_{(t_3,t_2)}^{(n-2)}|g\rangle \right\} \langle g|U_{(t_1,0)}^{(1)}|g\rangle + \dots \\
& = P_n^{I_2} \langle g|U_{(t_1,0)}^{(0)}|g\rangle + P_{n-1}^{I_2} \langle g|U_{(t_1,0)}^{(1)}|g\rangle + \dots = \sum_{\alpha=0}^n P_{n-\alpha}^{I_2} \langle g|U_{(t_1,0)}^{(\alpha)}|g\rangle, \quad (61)
\end{aligned}$$

Similar manipulations with the second two terms lead to :

$$\sum_{\alpha=0}^{n-1} \langle g|U_{(t_3,t_2)}^{(n-\alpha-1)}|g\rangle \langle e|U_{(t_1,0)}^{(\alpha)}|g\rangle + \sum_{\alpha=0}^{n-2} \langle e|U_{(t_3,t_2)}^{(n-\alpha-2)}|g\rangle \langle e|U_{(t_1,0)}^{(\alpha)}|g\rangle = \sum_{\alpha=0}^{n-1} P_{n-1-\alpha}^{I_2} \langle e|U_{(t_1,0)}^{(\alpha)}|g\rangle \quad (62)$$

Combining Eqs. (61) and (62) we get :

$$\begin{aligned}
& \sum_{\alpha=0}^n P_{n-\alpha}^{I_2} \langle g|U_{(t_1,0)}^{(\alpha)}|g\rangle + \sum_{\alpha=0}^{n-1} P_{n-1-\alpha}^{I_2} \langle e|U_{(t_1,0)}^{(\alpha)}|g\rangle = \\
& P_n^{I_2} \langle g|U_{(t_1,0)}^{(0)}|g\rangle + \left\{ P_{n-1}^{I_2} \langle e|U_{(t_1,0)}^{(0)}|g\rangle + P_{n-1}^{I_2} \langle g|U_{(t_1,0)}^{(1)}|g\rangle \right\} + \left\{ P_{n-2}^{I_2} \langle e|U_{(t_1,0)}^{(1)}|g\rangle + P_{n-2}^{I_2} \langle g|U_{(t_1,0)}^{(2)}|g\rangle \right\} + \dots = \sum_{\alpha=0}^n P_{n-\alpha}^{I_2} P_{\alpha}^{I_1} \quad (63)
\end{aligned}$$

Now we concentrate on the terms multiplied by the factor $e^{-\Gamma\Delta}$ in Eq. (60). Let's add and subtract the two following terms :

$$\sum_{\alpha=0}^n \langle g|U_{(t_3,t_2)}^{(n-\alpha)}|g\rangle \langle g|U_{(t_1,0)}^{(\alpha)}|g\rangle + \sum_{\alpha=0}^{n-1} \langle e|U_{(t_3,t_2)}^{(n-\alpha-1)}|g\rangle \langle g|U_{(t_1,0)}^{(\alpha)}|g\rangle.$$

We get

$$e^{-\Delta\Gamma} \left\{ \sum_{\alpha=0}^n \langle g|U_{(t_3,t_2)}^{(n-\alpha)}|e\rangle \langle e|U_{(t_1,0)}^{(\alpha)}|g\rangle + \sum_{\alpha=0}^{n-1} \langle e|U_{(t_3,t_2)}^{(n-\alpha-1)}|e\rangle \langle e|U_{(t_1,0)}^{(\alpha)}|g\rangle + \sum_{\alpha=0}^n \langle g|U_{(t_3,t_2)}^{(n-\alpha)}|g\rangle \langle g|U_{(t_1,0)}^{(\alpha)}|g\rangle \right\}$$

$$\begin{aligned}
& + \sum_{\alpha=0}^{n-1} \langle e | U_{(t_3, t_2)}^{(n-\alpha-1)} | g \rangle \langle g | U_{(t_1, 0)}^{(\alpha)} | g \rangle - \sum_{\alpha=0}^n \langle g | U_{(t_3, t_2)}^{(n-\alpha)} | g \rangle \langle g | U_{(t_1, 0)}^{(\alpha)} | g \rangle - \sum_{\alpha=0}^{n-1} \langle e | U_{(t_3, t_2)}^{(n-\alpha-1)} | g \rangle \langle g | U_{(t_1, 0)}^{(\alpha)} | g \rangle \\
& - \sum_{\alpha=0}^{n-1} \langle g | U_{(t_3, t_2)}^{(n-\alpha-1)} | g \rangle \langle e | U_{(t_1, 0)}^{(\alpha)} | g \rangle - \sum_{\alpha=0}^{n-2} \langle e | U_{(t_3, t_2)}^{(n-\alpha-2)} | g \rangle \langle e | U_{(t_1, 0)}^{(\alpha)} | g \rangle \Big\} \quad (64)
\end{aligned}$$

But the first 4 paths of Eq. (64) are just the semiclassical part of probability of emitting n photons from the two pulses attached together

$$P_n^{Cla, I_2 I_1} = \sum_{\alpha=0}^n \langle g | U_{(t_3, t_2)}^{(n-\alpha)} (|g\rangle\langle g| + |e\rangle\langle e|) U_{(t_1, 0)}^{(\alpha)} | g \rangle + \sum_{\alpha=0}^{n-1} \langle e | U_{(t_3, t_2)}^{(n-1-\alpha)} (|g\rangle\langle g| + |e\rangle\langle e|) U_{(t_1, 0)}^{(\alpha)} | g \rangle \quad (65)$$

(compare with Eq. (16)). And the last 4 paths of Eq. (64) are equal to Eq. (61)+Eq. (62). Putting all this information together we obtain

$$P_n = \sum_{\alpha=0}^n P_{n-\alpha}^{I_2} P_{\alpha}^{I_1} + e^{-\Delta\Gamma} \left\{ P_n^{Cla, I_2 I_1} - \sum_{k=0}^n P_{n-\alpha}^{I_2} P_{\alpha}^{I_1} + (e^{\Delta(\Gamma/2+i\omega_0)} A_n^{\text{Coh}} + C.C.) \right\} \quad (66)$$

Finally, by addition and subtraction of the coherence trajectories:

$$\begin{aligned}
e^{-\Delta\Gamma} \{ A_n^{\text{Coh}, I_2 I_1} + C.C. \} &= e^{-\Delta\Gamma} \left\{ \sum_{\alpha=0}^n \langle g | U_{(t_3, t_2)}^{(n-\alpha)} (|c\rangle\langle c| + |c^*\rangle\langle c^*|) U_{(t_1, 0)}^{(\alpha)} | g \rangle + \sum_{\alpha=0}^{n-1} \langle e | U_{(t_3, t_2)}^{(n-1-\alpha)} (|c\rangle\langle c| + |c^*\rangle\langle c^*|) U_{(t_1, 0)}^{(\alpha)} | g \rangle \right\} \\
&= e^{-\Delta\Gamma} \{ A_n^{\text{Coh}} + C.C. \}
\end{aligned}$$

to $P_n^{Cla, I_2 I_1}$ we obtain Eq. (24). Using Eq. (24) it should be taken into account however that not all the coherence paths now oscillate in Δ with ω_0 .

APPENDIX B

The Rotating Wave Approximation (RWA) [21] consists of neglecting the non-resonant processes of rising from $|g\rangle$ to $|e\rangle$ by emitting a photon and falling from $|e\rangle$ to $|g\rangle$ by absorbing a photon. Switching to the rotating frame by applying the transformation $A_{(t-t', \phi, \omega_L)}$ defined below, it is possible to suppress any time dependence in the Bloch equation Eq. (1). As a result the following time independent equation is obtained

$$\dot{\tilde{\sigma}}_{(t)} = [\tilde{L} + \hat{\Gamma}] \tilde{\sigma}_{(t)} \quad (67)$$

where

$$\tilde{\sigma}_{(t)} = A_{(t-t', \phi, \omega_L)} \sigma_{(t)}, \quad (68)$$

t' - is the initial moment,

$$\tilde{L} = \begin{pmatrix} -\Gamma & 0 & \frac{-i\Omega}{2} & \frac{i\Omega}{2} \\ 0 & 0 & \frac{i\Omega}{2} & \frac{-i\Omega}{2} \\ \frac{-i\Omega}{2} & \frac{i\Omega}{2} & -\frac{\Gamma}{2} - i\delta_L & 0 \\ \frac{i\Omega}{2} & \frac{-i\Omega}{2} & 0 & -\frac{\Gamma}{2} + i\delta_L \end{pmatrix} \quad (69)$$

and the transformation $A_{(t-t', \phi, \omega_L)}$ is given by

$$A_{(t-t', \phi, \omega_L)} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & e^{-i(\omega_L(t-t')+\phi)} & 0 \\ 0 & 0 & 0 & e^{i(\omega_L(t-t')+\phi)} \end{pmatrix}, \quad (70)$$

where ϕ is the phase of the laser at the initial moment t' . In the new representation the calculation of the Green function is straightforward (see Eq. (74)). Representing the solution to the time independent Bloch equation Eq. (67) in the rotating frame as the infinite iterative expansion in $\hat{\Gamma}$ we find the following expression for n -photon-propagator within RWA

$$\tilde{U}_{(t-t')}^{(n)} = \int_{t'}^t \cdots \int_{t'}^{t_2} \tilde{\mathcal{G}}(t-t_n) \hat{\Gamma} \cdots \hat{\Gamma} \tilde{\mathcal{G}}(t_1-t') dt_1 \cdots dt_n. \quad (71)$$

Hence

$$\tilde{\sigma}_{(t)}^{(n)} = \tilde{U}_{(t-t')}^{(n)} \tilde{\sigma}_{(t')}. \quad (72)$$

where $\tilde{\sigma}_{(t')} = A_{(0, \phi, \omega_L)} \sigma_{(t')}$ is the initial condition. Finally for obtaining $\sigma_{(t)}^{(n)}$ we have to apply the inverse

transformation

$$\sigma_{(t)}^{(n)} = A_{(t-t', \phi, \omega_L)}^{-1} \tilde{U}_{(t-t')}^{(n)} A_{(0, \phi, \omega_L)} \sigma_{(t')} \quad (73)$$

From Eq. (73) one easily makes the following conclusions: (i) the initial state of the molecule is multiplied by $A_{(0, \phi_1, \omega_L)}$, where ϕ_1 is the initial phase of the laser at the beginning of the first pulse, which shifts the initial coherence phase by $-\phi_1$ (ii) the delay period propagators are now multiplied by $A_{(0, \phi_2, \omega_L)}$ from the left due to the second pulse and by $A_{(T, \phi_1, \omega_L)}^{-1}$ from the right due to the first pulse (ϕ_2 is the initial laser phase at the beginning of the second pulse). Clearly, this leads only to an additional phase shift ($T\omega_L + \phi_1 - \phi_2$) of the coherence terms. Therefore calculating the photon statistics for the square pulses we rewrite the Eqs. (20),(21),(22) with the following modifications:

1) In the definition of the n-photon-propagator Eq. (7) the Green function defined as the time ordered exponential are replaced by

$$\tilde{\mathcal{G}}(t - t') = \exp \left[(t - t') \tilde{L} \right] \quad (74)$$

which are Green functions for the time intervals inside the pulses within RWA.

2) The initial state of the system must be replaced by $A_{(0, \phi, \omega_L)} \sigma_{(0)}$

3) The coherent terms A_n^{Coh} are multiplied by additional phase factor $e^{i(\omega_L T + \phi_1 - \phi_2)}$.

Remark : If in experiments the initial phases of the pulses are random variables, it's necessary to replace all the phase factors with their ensemble averages.

Thus summarizing we have

$$P_n = p_n^{\text{Cla}} + e^{-\Delta\Gamma/2} \left[e^{i(\Delta+T)\omega_0 + \phi_1 - \phi_2} a_n^{\text{Coh}} + C.C. \right], \quad (75)$$

where

$$\begin{aligned} p_n^{\text{Cla}} = & \sum_{\alpha=0}^n \left\{ \langle g | \tilde{U}_{(t_3, t_2)}^{(n-\alpha)} | g \rangle \langle g | \tilde{U}_{(t_1, 0)}^{(\alpha)} | \tilde{g} \rangle + e^{-\Delta\Gamma} \langle g | \tilde{U}_{(t_3, t_2)}^{(n-\alpha)} | e \rangle \langle e | \tilde{U}_{(t_1, 0)}^{(\alpha)} | \tilde{g} \rangle \right\} + \sum_{\alpha=0}^{n-1} (1 - e^{-\Delta\Gamma}) \langle g | \tilde{U}_{(t_3, t_2)}^{(n-\alpha-1)} | g \rangle \langle e | \tilde{U}_{(t_1, 0)}^{(\alpha)} | \tilde{g} \rangle \\ & + \sum_{\alpha=0}^{n-1} \left\{ \langle e | \tilde{U}_{(t_3, t_2)}^{(n-\alpha-1)} | g \rangle \langle g | \tilde{U}_{(t_1, 0)}^{(\alpha)} | \tilde{g} \rangle + e^{-\Delta\Gamma} \langle e | \tilde{U}_{(t_3, t_2)}^{(n-\alpha-1)} | e \rangle \langle e | \tilde{U}_{(t_1, 0)}^{(\alpha)} | \tilde{g} \rangle \right\} + \sum_{\alpha=0}^{n-2} (1 - e^{-\Delta\Gamma}) \langle e | \tilde{U}_{(t_3, t_2)}^{(n-\alpha-2)} | g \rangle \langle e | \tilde{U}_{(t_1, 0)}^{(\alpha)} | \tilde{g} \rangle \end{aligned} \quad (76)$$

and

$$a_n^{\text{Coh}} = \sum_{\alpha=0}^n \langle g | \tilde{U}_{(t_3, t_2)}^{(n-\alpha)} | c \rangle \langle c | \tilde{U}_{(t_1, 0)}^{(\alpha)} | \tilde{g} \rangle + \sum_{\alpha=0}^{n-1} \langle e | \tilde{U}_{(t_3, t_2)}^{(n-\alpha-1)} | c \rangle \langle c | \tilde{U}_{(t_1, 0)}^{(\alpha)} | \tilde{g} \rangle, \quad (77)$$

with $|\tilde{g}\rangle = A_{(0, \phi_1, \omega_L)} |g\rangle$.

APPENDIX C

Here we show the derivation of exact expressions for P_1 and P_2 for two equal square pulses obtained within RWA .

For P_1 : The one-photon-propagator in $(0, t)$ may be decomposed to the sum of 4 different terms

$$U_{(t, 0)}^{(1)} = \sum_{k=0}^1 \left[U_{(t, t_3)}^{(\alpha)} U_{(t_3, t_2)}^{(1-\alpha)} U_{(t_2, t_1)}^{(0)} U_{(t_1, 0)}^{(0)} + U_{(t, t_3)}^{(0)} U_{(t_3, t_2)}^{(0)} U_{(t_2, t_1)}^{(\alpha)} U_{(t_1, 0)}^{(1-\alpha)} \right] \quad (78)$$

Inserting the closure relation Eq. (15) between every two propagators of Eq. (78) and applying RWA we obtain the probability of emitting a single photon using the trajectories notation

$$p_1^{\text{Cla}} = \sum_{\alpha=0}^1 \left\{ \langle g | \tilde{U}_{t_3, t_2}^{(\alpha)} | g \rangle \langle g | \tilde{U}_{t_1, 0}^{(1-\alpha)} | g \rangle + \langle g | \tilde{U}_{t_3, t_2}^{(\alpha)} | e \rangle \langle e | \tilde{U}_{t_1, 0}^{(1-\alpha)} | g \rangle e^{-\Gamma\Delta} \right\}$$

$$+ \langle g | \tilde{U}_{t_3, t_2}^{(0)} | g \rangle \langle e | \tilde{U}_{t_1, 0}^{(0)} | g \rangle (1 - e^{-\Gamma \Delta}) + \langle e | \tilde{U}_{t_3, t_2}^{(0)} | e \rangle \langle e | \tilde{U}_{t_1, 0}^{(1-\alpha)} | g \rangle e^{-\Gamma \Delta} + \langle e | \tilde{U}_{t_3, t_2}^{(0)} | g \rangle \langle g | \tilde{U}_{t_1, 0}^{(0)} | g \rangle. \quad (79)$$

$$a_1^{\text{Coh}} = \sum_{\alpha=0}^1 \langle g | \tilde{U}_{t_3, t_2}^{(\alpha)} | c \rangle \langle c | \tilde{U}_{t_1, 0}^{(1-\alpha)} | g \rangle + \langle e | \tilde{U}_{t_3, t_2}^{(0)} | c \rangle \langle c | \tilde{U}_{t_1, 0}^{(0)} | g \rangle. \quad (80)$$

After some tedious algebra using Eqs. (3), (69), (71), (74) we finally obtain :

$$P_1 = a_1 + b_1 e^{-\Delta} + c_1 e^{-\frac{\Delta}{2}} \cos[\omega_0 (T + \Delta)]. \quad (81)$$

Where

$$a_1 = \frac{e^{-T}}{16y^7} (1 - y^2) \left[a_{11} + a_{12} \cosh\left(\frac{T y}{2}\right) + a_{13} \sinh\left(\frac{T y}{2}\right) + a_{14} \cosh(T y) + a_{15} \sinh(T y) \right]. \quad (82)$$

$$y = \sqrt{1 - 4\Omega^2}, \quad (83)$$

$$a_{11} = y(y^2 - 1) [4(y^2 - 3) + 3T(y^2 - 1)], a_{12} = -2y(Ty^4 + 8y^2 - T - 16), a_{13} = 4[-(T + 3)y^4 + (T + 4)y^2 + 3], \\ a_{14} = (T + 4)y^5 + 6Ty^3 + (T - 20)y, a_{15} = 2[(2T + 5)y^4 + 2(T - 5)y^2 - 3].$$

$$b_1 = \frac{e^{-T}}{16y^7} (1 - y^2)^3 \left[-3Ty + 2Ty \cosh\left(\frac{T y}{2}\right) + 12 \sinh\left(\frac{T y}{2}\right) + Ty \cosh(T y) - 6 \sinh(T y) \right]. \quad (84)$$

And

$$c_1 = \frac{e^{-T}}{16y^7} (1 - y^2) \left[c_{11} + c_{12} \cosh\left(\frac{T y}{2}\right) + c_{13} \sinh\left(\frac{T y}{2}\right) + c_{14} \cosh(T y) + c_{15} \sinh(T y) \right]. \quad (85)$$

$$c_{11} = -2y [2(y^4 - 3) + T(y^4 + 2y^2 - 3)], c_{12} = 4y [(T + 4)y^2 - T - 8], c_{13} = 4 [Ty^4 + (2 - T)y^2 - 6], \\ c_{14} = 2y [(T + 2)y^4 - 8y^2 - T + 10], c_{15} = 4 [Ty^4 - (T + 1)y^2 + 3].$$

For P_2 :

The two-photon-propagator may be decomposed to the sum of 10 terms.

$$U_{(t,0)}^{(2)} = \sum_{\alpha=0}^2 \left[U_{(t,t_3)}^{(0)} U_{(t_3,t_2)}^{(\alpha)} U_{(t_2,t_1)}^{(0)} U_{(t_1,0)}^{(2-\alpha)} + U_{(t,t_3)}^{(\alpha)} U_{(t_3,t_2)}^{(0)} U_{(t_2,t_1)}^{(2-\alpha)} U_{(t_1,0)}^{(0)} \right] + \sum_{\beta,\alpha=0}^1 U_{(t,t_3)}^{(\beta)} U_{(t_3,t_2)}^{(\alpha)} U_{(t_2,t_1)}^{(1-\beta)} U_{(t_1,0)}^{(1-\alpha)} \quad (86)$$

(Since $U_{t_2, t_1}^{(2)} = 0$ there are only 8 non-zero terms.) This leads to the following expressions for P_2^{Cla} and A_2^{Coh} :

$$p_2^{\text{Cla}} = \sum_{k=0}^2 \left\{ \langle g | \tilde{U}_{(t_3, t_2)}^{(k)} | g \rangle \langle g | \tilde{U}_{(t_1, 0)}^{(2-k)} | g \rangle + \langle g | \tilde{U}_{(t_3, t_2)}^{(k)} | e \rangle \langle e | \tilde{U}_{(t_1, 0)}^{(2-k)} | g \rangle e^{-\Gamma \Delta} \right\} + \langle e | \tilde{U}_{(t_3, t_2)}^{(0)} | g \rangle \langle e | \tilde{U}_{(t_1, 0)}^{(0)} | g \rangle (1 - e^{-\Gamma \Delta})$$

$$+ \sum_{k=0}^1 \left\{ \langle g | \tilde{U}_{(t_3, t_2)}^{(k)} | g \rangle \langle e | \tilde{U}_{(t_1, 0)}^{(1-k)} | g \rangle (1 - e^{-\Gamma \Delta}) + \langle e | \tilde{U}_{(t_3, t_2)}^{(k)} | g \rangle \langle g | \tilde{U}_{(t_1, 0)}^{(1-k)} | g \rangle + \langle e | \tilde{U}_{(t_3, t_2)}^{(k)} | e \rangle \langle e | \tilde{U}_{(t_1, 0)}^{(1-k)} | g \rangle e^{-\Gamma \Delta} \right\}$$

$$a_2^{\text{Coh}} = \sum_{k=0}^2 \langle g | \tilde{U}_{(t_3, t_2)}^{(k)} | c \rangle \langle c | \tilde{U}_{(t_1, 0)}^{(2-k)} | g \rangle + \sum_{k=0}^1 \langle e | \tilde{U}_{(t_3, t_2)}^{(k)} | c \rangle \langle c | \tilde{U}_{(t_1, 0)}^{(1-k)} | g \rangle + \text{C.C.} \quad (87)$$

Calculating the matrix elements with the help of Mathematica yields:

$$P_2 = a_2 + b_2 e^{-\Delta} + c_2 e^{-\frac{\Delta}{2}} \cos[\omega_0 (T + \Delta)]. \quad (88)$$

where

$$a_2 = \frac{e^{-T}}{64y^{10}} (y^2 - 1)^2 \left[a_{21} + a_{22} \cosh\left(\frac{Ty}{2}\right) + a_{23} \sinh\left(\frac{Ty}{2}\right) + a_{24} \cosh(Ty) + a_{25} \sinh(Ty) \right]. \quad (89)$$

$$\begin{aligned} a_{21} &= (9T^2 + 40T + 24) y^6 - 2(9T^2 + 56T + 17) y^4 + 9(T^2 + 8T - 12) y^2 + 126, \\ a_{22} &= (T^2 - 32) y^6 + 4(T + 32) y^4 - (T^2 + 20T + 64) y^2 - 192, \\ a_{23} &= 2y[(y^2 - 1)T^2 y^2 + T(3y^4 - 8y^2 - 3) - 4(8y^4 - 39y^2 + 51)], \\ a_{24} &= (T^2 + 8T + 8) y^6 + 2(3T^2 - 6T - 47) y^4 + (T^2 - 52T + 172) y^2 + 66, \\ a_{25} &= y[4(y^2 + 1)T^2 y^2 + (17y^4 - 58y^2 - 15)T - 4(4y^4 + 9y^2 - 51)]. \end{aligned}$$

$$b_2 = \frac{e^{-T}}{64y^{10}} (y^2 - 1)^2 \left[b_{21} + b_{22} \cosh\left(\frac{Ty}{2}\right) + b_{23} \sinh\left(\frac{Ty}{2}\right) + b_{24} \cosh(Ty) + b_{25} \sinh(Ty) \right]. \quad (90)$$

$$\begin{aligned} b_{21} &= 3(3T^2 - 8) y^6 - 18(T^2 - 7) y^4 + 9(T^2 - 28) y^2 + 126, b_{22} = -(T^2 - 32) y^6 + 2(T^2 - 96) y^4 - (T^2 - 384) y^2 - 192, \\ b_{23} &= -6Ty(y^2 - 1)^2, b_{24} = (T^2 - 8) y^6 - 2(T^2 - 33) y^4 + (T^2 - 132) y^2 + 66, b_{25} = -15Ty(y^2 - 1)^2. \end{aligned}$$

And

$$c_2 = \frac{e^{-T}}{32y^{10}} (y^2 - 1)^2 \left[c_{21} + c_{22} \cosh\left(\frac{Ty}{2}\right) + c_{23} \sinh\left(\frac{Ty}{2}\right) + c_{24} \cosh(Ty) + c_{25} \sinh(Ty) \right], \quad (91)$$

$$\begin{aligned} c_{21} &= -T(T + 4)y^6 + 2(5T^2 + 12T - 15) y^4 - 3(3T^2 + 12T - 44) y^2 - 126, \\ c_{22} &= -(T^2 + 2T - 32) y^4 + (T^2 + 10T - 160) y^2 + 192, \\ c_{23} &= -(T^2 - 32) y^5 + (T^2 + 2T - 156) y^3 + 6(T + 34)y, \\ c_{24} &= T(T + 4)y^6 - 2(11T + 1)y^4 + (-T^2 + 26T + 28) y^2 - 66, \\ c_{25} &= y[2(y^2 - 1)T^2 y^2 + T(-3y^4 - 4y^2 + 15) - 2(8y^4 - 39y^2 + 51)]. \end{aligned}$$

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